

# Development of an electrode for lead–acid batteries possessing a high electrochemical utilization factor and invariable cycling characteristics

L.A. Yolshina \*, V.Ya. Kudyakov, V.G. Zyryanov

*Institute of High-Temperature Electrochemistry, Urals Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*

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## Abstract

Investigations have been carried out on the deposition of compact lead layers on the surfaces of various metallic substrates. It is shown that the lead coatings so obtained are non-uniform in thickness and feature high porosities. The lead-film electrode thus produced on the surface of a fine copper grid can be used as a positive electrode in the lead–acid battery.

*Keywords:* Lead–acid batteries; Lead battery plates

## 1. Introduction

The lead–acid battery has been the most popular and best studied of the electrochemical power sources. Nevertheless, during the last two decades, numerous attempts have been made to improve and perfect this battery, including the introduction of activating agents into the sulfuric acid electrolyte [1] or reduction of battery mass by replacement of heavy and costly lead grids [2]. In particular, the deposition of lead dioxide from lead nitrate solution onto a platinum substrate has become a classical experiment [3]. The electrodes thus obtained exhibit poor adhesion of the coating to the metallic substrate, resulting in inhibition of electrochemical discharge due to the emergence of coarse  $\text{PbSO}_4$  crystals under the lead dioxide film.

We have conducted a special study of the deposition of lead onto various substrates such as aluminum, commercial titanium (99.5%), titanium alloy grade OT4 (Al 3–4.5%, Mn 0.8–2%), nickel, zirconium, copper, a number of stainless steels (Cr 13% and Cr 18%, Ni 10%, Ti 1%), as well as onto the same steels and titanium alloy OT4 after they have been preliminarily coated with copper from a melt composed of predominantly cuprous chloride and chlorides of alkali or alkali-earth metals at temperatures of 500–550°C for several minutes [4]. A lead coating on these metals was obtained by a currentless, contact-exchange method from a chloride melt of complex composition containing  $\text{Pb}^{2+}$  ions at temperatures considerably exceeding the melting temperature of lead.

According to X-ray phase analysis, specific conditions can be created on all of the metals investigated by us, permitting a homogenous lead coating to be formed on the metal surface, permeated by numerous very fine pores which, however, do not reach the metal base (Fig. 1). The thickness of the lead coating, and the quantity and size of the pores depend on the nature of the metal, electrolyte composition, temperature and duration of the lead plating. Preliminary electrochemical tests have shown that the best characteristics are exhibited by a copper-base lead electrode. In chloride melts the difference between standard potentials of lead and copper is slight [5], thus hampering the formation of a lead coating. Lead is practically insoluble in copper, forming a low-melting eutectic, consisting practically of pure metal (lead content 99.94%) [6]. The escape of copper ions from the lead coating's pores into the acid electrolyte (in the case of an incomplete lead coating) is hampered by its positive standard potential in aqueous solutions of acids.

## 2. Experimental

Measurements were carried out in a standard electrochemical cell, with a porous glass diaphragm separating the cathodic region, in the potentiodynamic mode at a linear scanning rate of  $10 \text{ mV s}^{-1}$  and a holding time of 200 s at extreme potentials. A silver chloride electrode ( $\text{Ag}/\text{AgCl}/\text{saturated KCl}$  solution) served as reference. The auxiliary electrode was a platinum one. In all cases 4.57 M  $\text{H}_2\text{SO}_4$  (32 wt.%), 'extra pure' grade, was used as electrolyte.

\* Corresponding author.

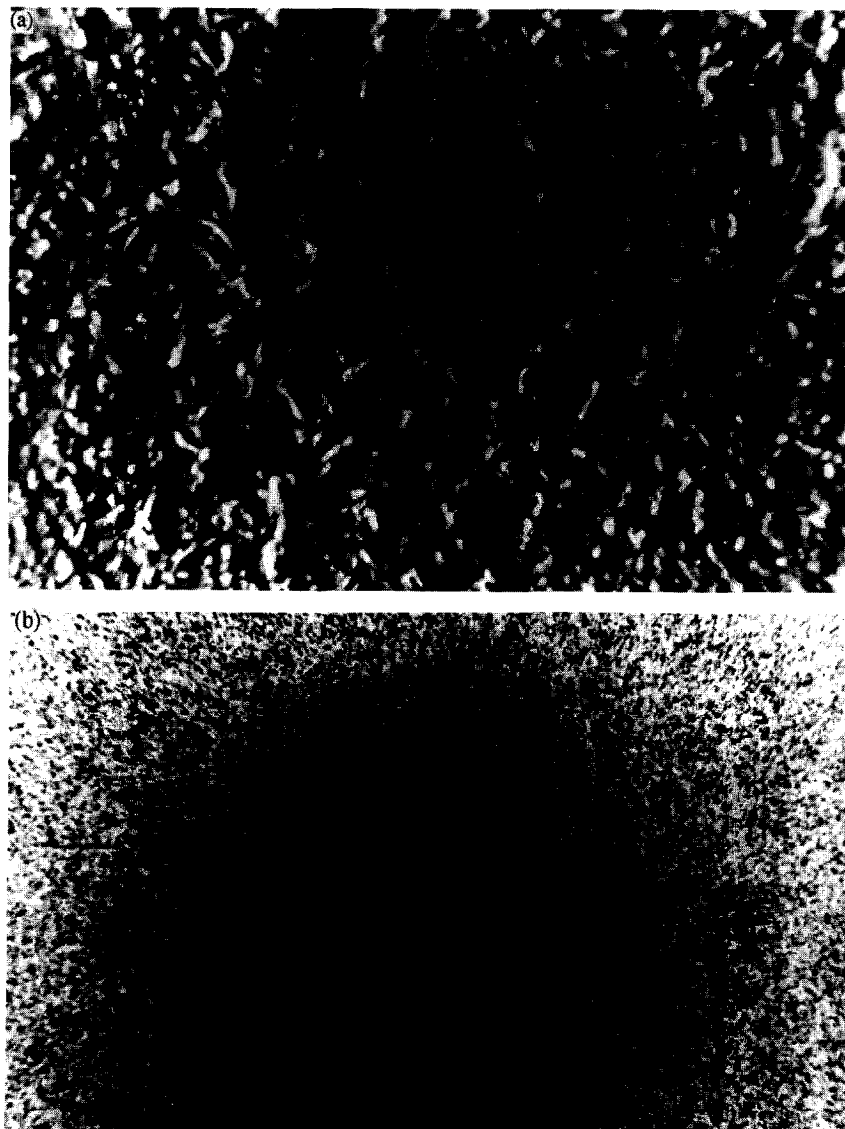


Fig. 1. Surface image of lead coating on copper ( $\times 2400$ ): (a) from the scanning electron micrograph; (b) in Pb  $M_{\alpha 1}$  rays.

Several types of lead electrodes were examined.

(i) A smooth lead-coated copper plate (Cu 99.99%).

(ii) A thick (0.5 mm) lead-coated copper grid (total impurities 0.05%) with an apparent electrode surface of 1.2 cm<sup>2</sup>.

(iii) A thin (0.2 mm) lead-coated copper grid (Cu base, Zn 0.009%, Al 0.005%, Sn 0.01%, Fe 0.005%, Si < 0.005%, Mn 0.001%, Ni 0.002%, total impurities 0.03%), with an apparent surface of 0.3 cm<sup>2</sup>.

(iv) Specimens of OT4 titanium alloy were preliminarily coated with copper from CuCl–MeCl melt and then with lead. Apparent surface was 2 cm<sup>2</sup>.

The lead coating was in all cases deposited as follows: a specimen, pickled for 20 s in a 20% solution of H<sub>2</sub>SO<sub>4</sub>, washed, and dried with acetone, was placed for 2–5 min in a molten chloride mix containing lead chloride. It was then washed thoroughly to remove salts.

A layer of lead dioxide was deposited on the electrodes during the first charge to 2.0 V in 32% H<sub>2</sub>SO<sub>4</sub>.

Solid products of interaction between copper and the lead-containing melt, as well as those of interaction between electrodes, were coated with a thin layer of lead, and sulfuric acid solutions, were analyzed with the help of a Camebax micro-X-ray spectrometer and a DRON-3 X-ray diffractometer. The escape of copper ions into the sulfuric acid solution was monitored by means of a Perkin-Elmer atomic-absorption spectrometer.

### 3. Results and discussion

Depending on the conditions of currentless deposition of lead, the coating thickness was 20–100 μm.

Profiles of lead distribution over the copper grid surface show that the lead coating has numerous pores with closed porosity (Fig. 2). The pores are regularly distributed over the entire electrode surface.

They are cylindrical in shape and their diameter is very small (between 0.2 and 0.5 μm). Thus, the actual surface area of a lead-film electrode may be hundred times as great

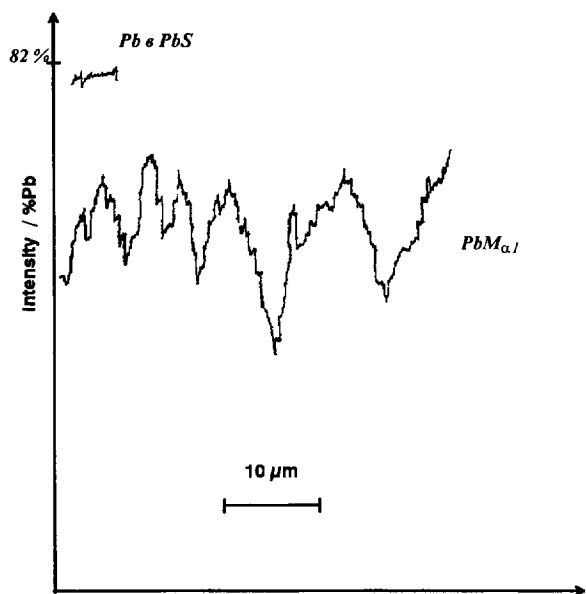


Fig. 2. Profile of lead distribution on surface of lead coating on copper before cycling (1:1).

as the apparent one. Nevertheless, in all cases, the current densities were calculated using the apparent electrode area. Fig. 3(a)–(c) shows typical volt-ampere diagrams during eight charge–discharge cycles.

Fig. 3(a) is for a lead-coated coarse copper grid, Fig. 3(b) for a lead-coated fine copper grid and Fig. 3(c) is for a lead-coated copper-plated OT4 titanium alloy. All were performed in dilute sulfuric acid solution over the potential range 0.7–2.0 V (relative to the silver chloride electrode).

It is apparent that the curves have similar shapes in all cases. Minimum current is observed during the first discharge. The discharge current peak occurs at the potential of 1.34 V in all cases. The discharge potential does not shift during cycling ( $n=20$ ). In cases (b) and (c), the current density increases up to the third cycle and then remains constant during the eighth to eighteenth cycles. The fact that discharging in all three cases takes place at the same value of the potential signifies that the electrochemical process is the same, namely, that  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$ . No escape of copper ions from the pores into sulfuric acid electrolyte was observed in the course of cycling. During electrochemical testing of the lead-film electrode made by lead plating of a thick copper film, we obtained a current density of 60–80  $\text{mA cm}^{-2}$ . In the case of lead plating of a thin copper film we obtained 290–350  $\text{mA cm}^{-2}$ , and 100–130  $\text{mA cm}^{-2}$  with the lead plating on a copper-plated titanium alloy (Table 1).

From the point of view of creating stable constructional materials, it seems promising to work on the improvement of the film electrode based on titanium and titanium alloys and having a two-layer copper/lead coating, since an electrode produced by direct lead plating of titanium does not exhibit such good properties.

Current density curves against time-into-discharge for a 2 V potential are presented in Fig. 4.

Table 1

Values of discharge current densities ( $\text{mA cm}^{-2}$ ) obtained at 1.34 V during cycling of lead-plated electrodes in  $\text{H}_2\text{SO}_4$

Cycle number	Fig. 3(a) Pb/coarse Cu grid	Fig. 3(b) Pb/fine Cu grid	Fig. 3(c) Pb/Cu/Ti alloy
1	–12.1	–13.7	–6.0
2	–45.0	–144.7	–103.3
3	–52.5	–193	–113
4	–61.7	–210.6	–117
5	–60	–238	–139
6	–52.5	–265.7	–160
7	–56.7	–257	–167
8	–58.3	–290	–170

The current at the start is at maximum in the first cycle, then its value becomes practically constant. At this potential, the current density stabilizes after 200 s.

We have attempted to determine the composition of phases present on the surface of the lead–copper film electrode during cycling in a sulfuric acid solution. For this purpose we took lead and sulfur distribution profiles of the electrode surfaces, when withdrawn from cycling at various potentials. Then recalculation was made of the % of  $\text{PbO}_2$  and  $\text{PbSO}_4$  in the surface film (see Table 2). It is shown that not all the lead dioxide takes part in the discharge reaction; its content at all potentials was not less than 50%. 75–80% of the surface is occupied by lead dioxide in the potential range 1.6–2.0 V. The lead distribution profile for the electrode surface (Fig. 5) shows that after 20 charge–discharge cycles the electrode surface remains porous, the pores not reaching the copper surface.

Metallographic data show that the coating of lead on copper after potentiodynamic cycling in sulfuric acid appears as follows: a porous and very irregular in thickness layer of lead is directly next to the copper surface, then follows an intermediate, discontinuous, layer of lead sulfate 0.9–6.0  $\mu\text{m}$  thick. The outermost layer (directly in contact with the sulfuric acid solution) is dense, uniform, lead dioxide (Fig. 6).

It was evident that, in the present case, there is no formation on the electrode surface of coarse lead sulfate crystals that could impede further discharge in the course of cycling.

Nevertheless, the utilization factor of useful substances could be increased at the expense of the formation of thicker and denser lead dioxide layers on the lead surface.

Table 2

Percentage composition of the outer coating of lead plating on the base of a fine copper grid during cycling in sulfuric acid

Potential (V)	% $\text{PbO}_2$	% $\text{PbSO}_4$
2.0	78.4	33.3
1.6	73.8	22.8
1.5	57.6	34.0
1.1	47.8	46.7
0.7	52.4	39.5

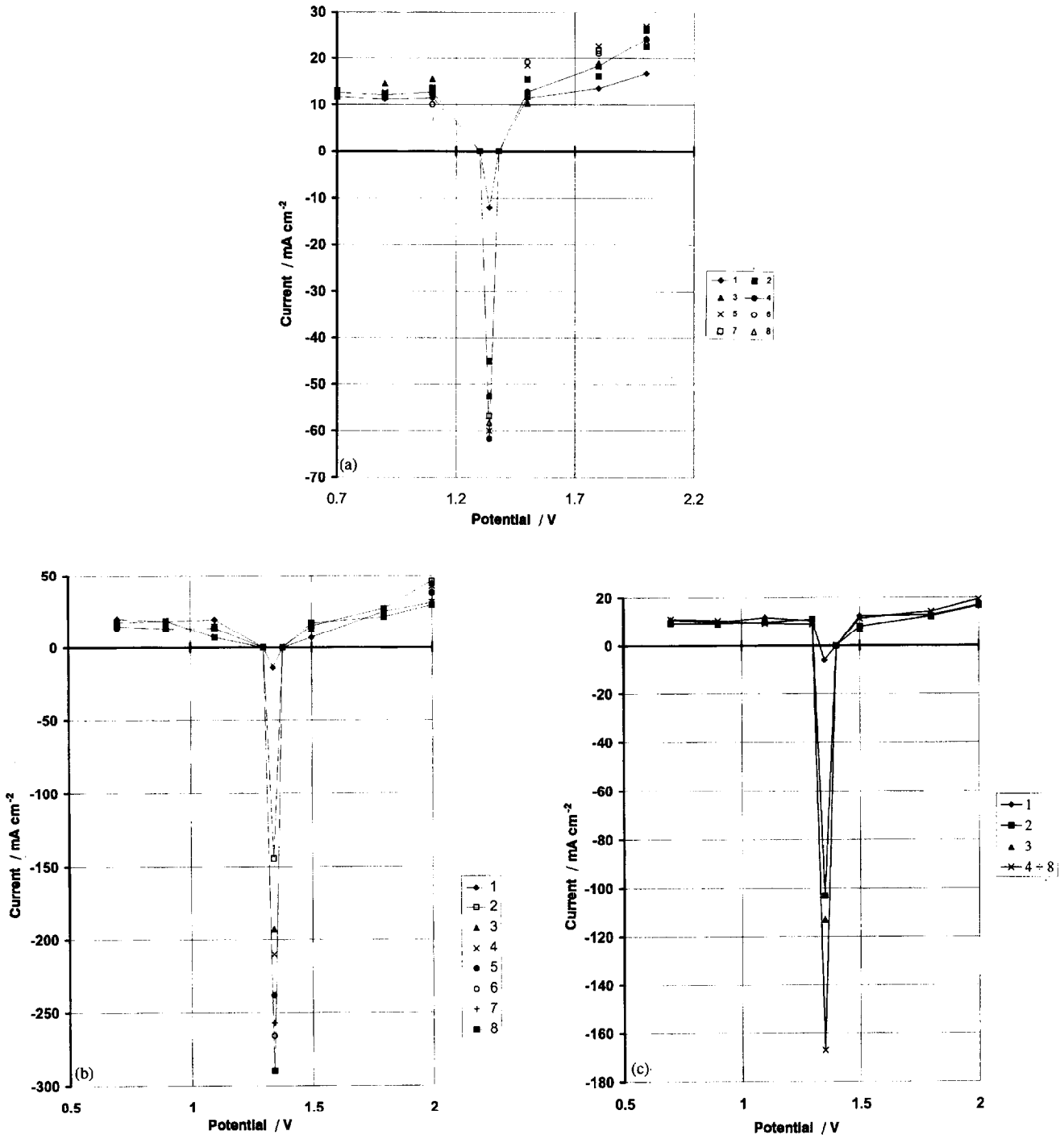


Fig. 3. Voltammograms between 0.7 and 2.2 V (vs. Ag/AgCl reference electrode) of: (a) lead on a coarse copper grid; (b) lead on a fine copper grid; (c) lead on a copper-plated titanium alloy. All in 32% H<sub>2</sub>SO<sub>4</sub>.

#### 4. Conclusions

Homogeneous lead coatings on a number of metals, such as Al, Ti, Zr, Ni, Cu and stainless steels, as well as on steels and titanium alloys preliminarily plated with copper by a contact exchange method have been obtained from chloride

melts. These differ considerably in thickness but feature a very high closed porosity.

Such lead films can be used in the lead–acid battery as positive electrodes as they permit one to attain high values of discharge current density.

The best electrochemical characteristics are exhibited by the film electrode obtained by lead plating a fine copper grid

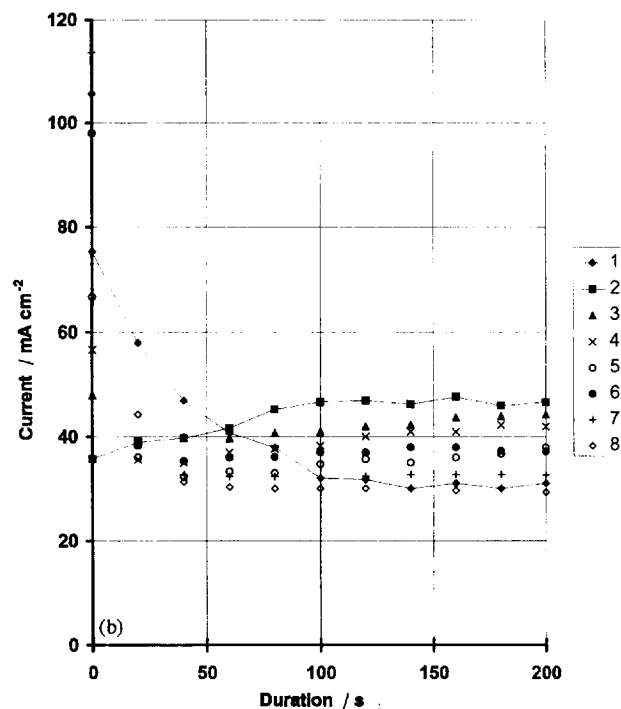
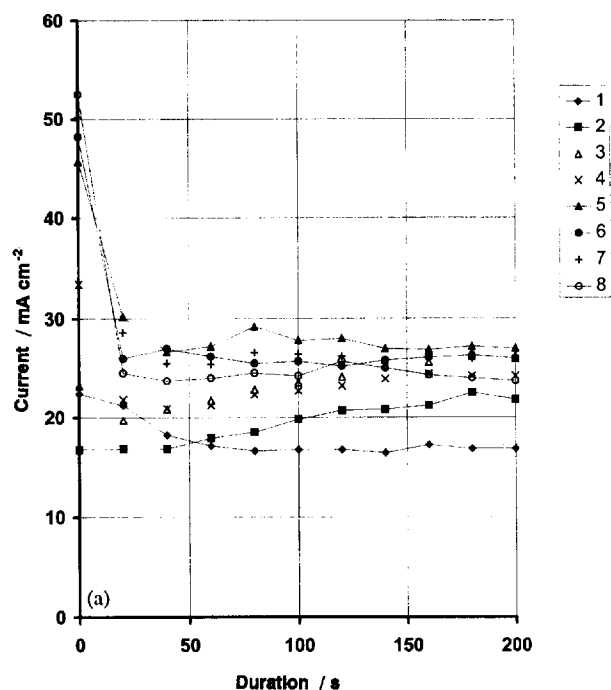


Fig. 4. Change in current density at 2 V with time of: (a) lead on a coarse copper grid. (b) lead on a fine copper grid. Both in 32%  $H_2SO_4$ .

in a melt containing lead chloride. The discharge current density on such an electrode attains  $350 \text{ mA cm}^{-2}$ .

It has been shown that, in the course of potentiodynamic charge–discharge cycling, a discontinuous lead sulfate layer is formed under the lead dioxide layer, this not impeding further recharge of the electrode.

Further work on the improvement of the lead-film electrode, that is the one on copper-plated titanium, shows great

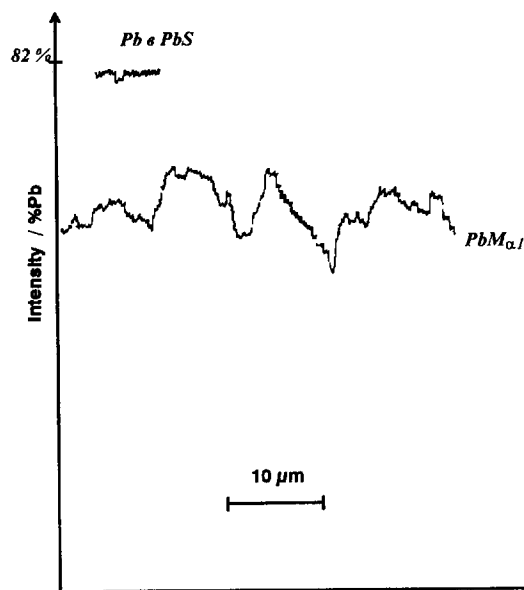


Fig. 5. Profile of lead distribution on surface of lead coating on copper electrode after 20 charge–discharge cycles (1:1).

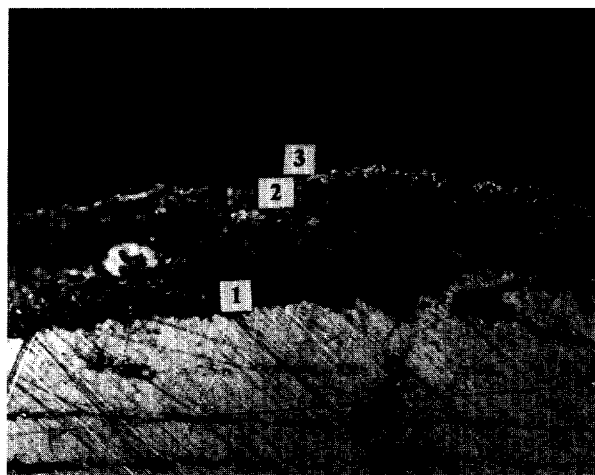


Fig. 6. Cross section ( $\times 630$ ) of a lead-film electrode at 1.6 V (vs. Ag/AgCl reference electrode) after 20 cycles in 32%  $H_2SO_4$ . Substrate: copper. 1 = Pb; 2 =  $PbSO_4$ ; 3 =  $PbO_2$ .

promise because of the higher constructional strength and lesser weight of the latter in relation to copper.

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